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Discovery of Dumbbell-Shaped $CsHe_n$ Exciplexes in Solid ^4He

D. Nettels, A. Hofer, P. Moroshkin,* R. Müller-Siebert, S. Ulzega, and A. Weis
Département de Physique, Université de Fribourg, Chemin du Musée 3, 1700 Fribourg, Switzerland †
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We have observed several new spectral features in the fluorescence of cesium atoms implanted in the hcp phase of solid helium following laser excitation to the 6^2P states. Based on calculations of the emission spectra using semiempirical Cs-He pair potentials the newly discovered lines can be assigned to the decay of specific Cs*Henexciplexes: an apple-shaped $Cs(A\Pi_{3/2})He_2$and a dumbbell-shaped $Cs(A\Pi_{1/2})He_n$ exciplex with a well-defined number n of bound helium atoms. While the former has been observed in other environments, it was commonly believed that exciplexes with n>2might not exist. The calculations suggest $Cs(A\Pi_{1/2})He_7$ to be the most probable candidate for that exciplex, in which the helium atoms are arranged on a ring around the waist of the dumbbell-shaped electronic density distribution of the cesium atom.

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Alkali atoms and helium atoms in their ground states strongly repel each other at small interatomic distances by virtue of the Pauli principle. However, an alkali atom excited to one of its P states can exert an attractive poten-tial on a helium atom that can lead to bound states, known as exciplexes. The formation of alkali-helium exciplexes was considered for the first time by Dupont-Roc [1] and Karnosky et al. [2] as an explanation for the quenching of atomic fluorescence from light alkali atoms (Na, Li) embedded in liquid or solid ^4He. In the meantime such molecules have been observed in different environ-ments, such as liquid helium and cold helium gas well as on the surface of helium nanodroplets. Here we present the first observations of such exciplexes in a solid helium matrix.

The maximum number of helium atoms for different alkali-helium exciplexes was found previously to be $n_{max}= 4$ for Na^*He_n [5], $n_{max}= 6$ for $K^* He_n$ [5] and Rb^*He_n [6] and $n_{max} = 2$ for Cs^*He_n[3]. Hirano et al. [3] discuss on the basis of Cs^*He_2-He potential energy surfaces that there should he no stable Cs^*He_3 configuration. They therefore conclude that exciplexes with more than $n_{max}= 2$ do not exist, since they regard the exciplex formation as a sequential process ($Cs^* \rightarrow Cs^*He_1 \rightarrow ... \rightarrow Cs^*He_{n\,max}$). However, our experimental results demonstrate unamhiguously that in the hcp phase of solid helium $Cs(A\Pi_{1/2})He_n$, exciplexes with $n > 2$ are formed following the excitation of cesium atoms to the $6P_{3/2}$ state. From the relative integrated observed line intensities we conclude that the formation of those exciplexes is the most probable deexcitation channel of the $6P_{3/2}$ state.

In earlier experiments [2] we have studied the excitation and fluorescence spectra of atomic cesium implanted into the bcc and hcp phases of solid helium. It was found that excitation on the D, transition ($6S_{1/2}$-$6P_{1/2}$) results in atomic fluorescence at the same transition, blueshifted (with respect to the free Cs atom) by the interaction with the helium matrix. At the same time, excitation on the D_2 transition ($6S_{1/2}$-$6P_{3/2}$) produces merely a weak fluo-rescence on the *D1* emission line, which indicates that the $6P_{3/2}$ atoms are partly quenched into the $6P_{1/2}$ state, from which a stray fluorescence is observed. The main relaxation channel of the $6P_{3/2}$ state remained unknown. Recently, the extension of the spectral range of our detection system has

allowed us to discover several new emis-sion lines, redshifted with respect to the atomic fluorescence line. We attribute those lines to the formation and decay of Cs^*He_n exciplexes.

In the present experiment a ^4He matrix doped with Cs atoms was produced by the technique described in our earlier papers [10,11]. Data were taken in the hcp phase of solid ^4He at a temperature of 1.5 K and a pressure of 31.6 bar. For the excitation of the embedded atoms we used a single mode cw Ti : Al_2O_3 laser, pumped by a Nd : $YV0_3$ laser. The laser wavelength was tuned to the *D2* absorption line of cesium, whose resonance is shifted to 800 nm due to the influence of the surrounding helium matrix. The atomic fluorescence light from the sample volume (-3 mm^3) is detected by a fiher coupled optical spectrum analyzer (Ando Co. Ltd., AQ-6315A), which has a detection range of 350-1750 nm with a spectral resolution of about 5 nm.

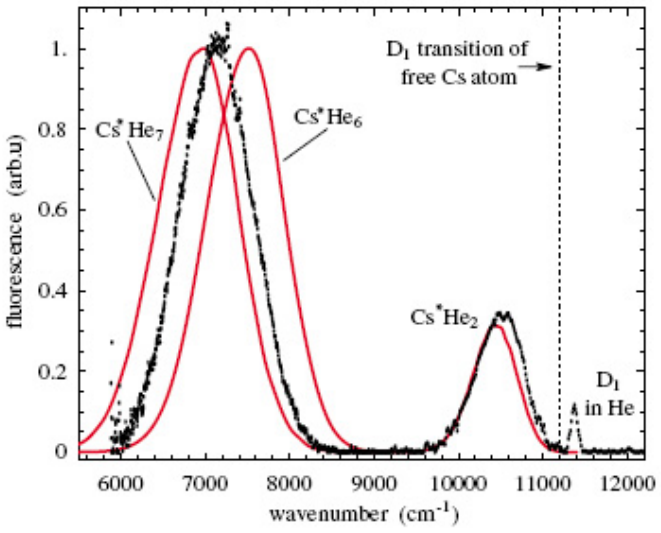

FIG. 1 (color online). Measured emission spectrum (dots) of matrix-isolated Cs atoms in the hcp phase of solid ^4He. The fluorescence emission was observed following resonant D_2 excitation of the atoms. For comparison, calculated emission lines (solid curves) of $Cs(A\Pi_{3/2})He_2$, $Cs(A\Pi_{3/2})He_6$, and $Cs(A\Pi_{1/2})He_7$ exciplexes are also presented.

Figure 1 shows a typical recorded emission spectrum, as well as calculated spectra of several Cs^*He_n exciplexes. The smallest peak at 11 400 cm-' corresponds to fluores-cence on the *D1* transition, indicating the existence of a weak transfer channel hetween the $6P_{3/2}$ and $6P_{1/2}$ states. That process was studied before in experiments with superfluid helium [12]. Another emission line appears at 10520 cm^{-1}. We attribute this broad and asymmetric peak to the emission of $Cs(A\Pi_{3/2})He_2$, exciplexes, which were previously observed in liquid helium and in cold helium gas [3]. The peak presented here is hlueshifted with respect to the one reported in [3] by approximately 500 cm^{-1}. That shift is due to the influence of the helium matrix and increases with helium pressure. The detailed study of the pressure shift in the hcc and hcp phases of solid helium will he presented elsewhere [13]. The most prominent emission line is found at 7130 cm^{-1} with a linewidth of 1010 cm^{-1} (FWHM) and integrated intensity almost 3 times stronger than the former peak. Our theoretical model suggests that this newly discovered intense emission line can he assigned to a higher order (n >2) exciplex.

We have calculated the emission spectra of Cs^*He_n exciplexes with a treatment analogous to those of [3,4]. We consider only the influence of the n helium atoms that form the exciplex and neglect the influence of the hulk of the surrounding helium matrix. The interaction hetween one cesium atom and the n He atoms is described as the sum over adiabatic molecular two-body interaction potentials. We use the pair potentials: V_σ^{6s} (r), V_σ^{6p} (r) and V_π^{6p} (r) calculated by Pascale [14]. For the *6S* ground state that potential, V_σ^{6s} (r), is radially symmetric. For the *6P* states the interaction is anisotropic and can he expressed by the operator

$$V^{6P}(\mathbf{r}) = V_{\sigma}^{6P}(r) + \left(\frac{\mathbf{L}\cdot\mathbf{r}}{\hbar r}\right)^2 [V_{\pi}^{6P}(r) - V_{\sigma}^{6P}(r)], \qquad (1)$$

where $\mathbf{r} = \mathbf{r}(r, \theta, \varphi)$ denotes the position vector of the helium atom with respect to the cesium atom and L is the orbital angular momentum operator of the cesium valence electron [l]. Stable exciplexes of the form $Cs^*He_{n=2}$ are formed by two helium atoms located on a common axis on opposite sides of the cesium atom. For $Cs^*He_{n>=3}$ the helium atoms are distributed on a concentric ring around the alkali atom. The summation over the pair potentials can he expressed by the operator $V_n^{Cs\text{-}He}(r) = \sum_{i=1}^{n} V^{6P}(\mathbf{r}i)$, with $\mathbf{r}i = \mathbf{r}(r, \theta=\pi/2, \varphi i = i2\pi/n)$ and n = 1,2,. . .. In addition we include He-He interactions by summing over the corresponding $V_{He\text{-}He}(R)$ potentials between neighboring helium atoms using the ab initio potential given by Aziz [15]. The distance R between two neighboring helium atoms is a function of the cesium-helium separation r and the number n of helium atoms: $R = |\mathbf{r}_i - \mathbf{r}_{i+1}| = 2r\sin(\pi/n)$. After including the spin-orbit interaction in Cs the total interaction potential of the Cs'He, system reads

$$V_{Cs^*He_n}(r) = V_n^{Cs\text{-}He}(r) + nV_{He\text{-}He}(R) + 2/3\Delta\mathbf{L}\cdot\mathbf{S}, \quad (2)$$

where $\Delta = 554.0\ cm^{-1}$ is the fine-structure splitting of the free cesium *6P* state and *S* the electronic spin operator. $V_{Cs^*Hen}(r)$ is diagonalized algebraically.

In Figures 2 and 3 the resulting r dependencies of the eigenvalues are shown for Cs^*He_2 and Cs^*He_7 respectively. The same plots also show the ground state potentials given by $n\,V_{\sigma}^{6s}(r) + nV_{He\text{-}He}(R)$. The quantization axis is defined by the symmetry axis of the exciplexes, which is the internuclear axis of the cesium atom and the two helium atoms in the case $Cs^*He_{n=1,2}$ whereas for $Cs^*He_{n>=3}$, it is the symmetry axis of the helium ring. Although the standard spectroscopic notations: $X^2\Sigma_{1/2}$, $A^2\Pi_{1/2}$, $A^2\Pi_{3/2}$, and $B^2\Sigma_{1/2}$ apply only for linear molecules, we retain that notation for simplicity to label all exciplexes. Pictographs next to the curves show the variation of the cesium electronic density as the *n* helium atoms, indicated by two filled circles, approach the cesium atom.

From the adiabatic potentials of Fig. 2 one sees that the helium atoms are repelled by the cesium valence electron. However, when two helium atoms approach along a nodal line of an apple-shaped electron distribution ($A^2\Pi_{3/2}$, configuration) they experience an attractive van der Waals force until they are repelled by the cesium core. This van der Waals attraction results in formation of $Cs(A\Pi_{3/2})He_2$, molecules, with a fluorescence spectrum centered at $10520\ cm^{-1}$.

For $Cs^*He_{n>=3}$ the situation is more complicated. There are no attractive minima in the potential curves correlated with $6P_{3/2}$ state of the cesium atom (see Fig. 3). However, as pointed out before, there exists a fine-structure relaxation channel from the $6P_{3/2}$ to the $6P_{1/2}$ state. When some helium atoms are positioned next to the cesium atom the electronic wave function of $6P_{1/2}$ state is deformed and looses its spherical symmetry. In the case of more than two helium atoms, it becomes dumbbell shaped (Fig. 3). Helium atoms are then attracted by van der Waals force along its nodal plane and may form an exciplex with n >2. With an increasing number of helium atoms around the waist of the dumbbell the repulsive potential between those atoms increases, which puts a natural limit on the maximum number n_{max} that can be accommodated. Emission lines of these exciplexes are further redshifted with respect to $Cs(A\Pi_{3/2})He_2$ and were never observed before.

One can see in Figs. 2 and 3 the potential barrier associated with the transformation of the $6P_{1/2}$ electron distribution from spherical to apple or dumbbell shaped. It was pointed out by Dupont-Roc [1] that the height of the potential barrier is determined by the strength of the spin-orbit interaction of the P state. If the L-S coupling is weak compared to the alkali-helium interaction as in the case of the light alkalis, it can be neglected and the electronic configuration can be approximated by $P_{x,y,z}$, orbitals that allows the formation of dumbbell-shaped exciplexes with n > 2. If on the other hand the spin-orbit interaction dominates, as for cesium, one has to consider the electron distribution of the L-S-coupled $P_{1/2}$ state, which is spherical and hence repulsive. In contrast to this simple model our treatment takes into account that the electronic configuration changes adiabatically its shape as the helium atoms approach.

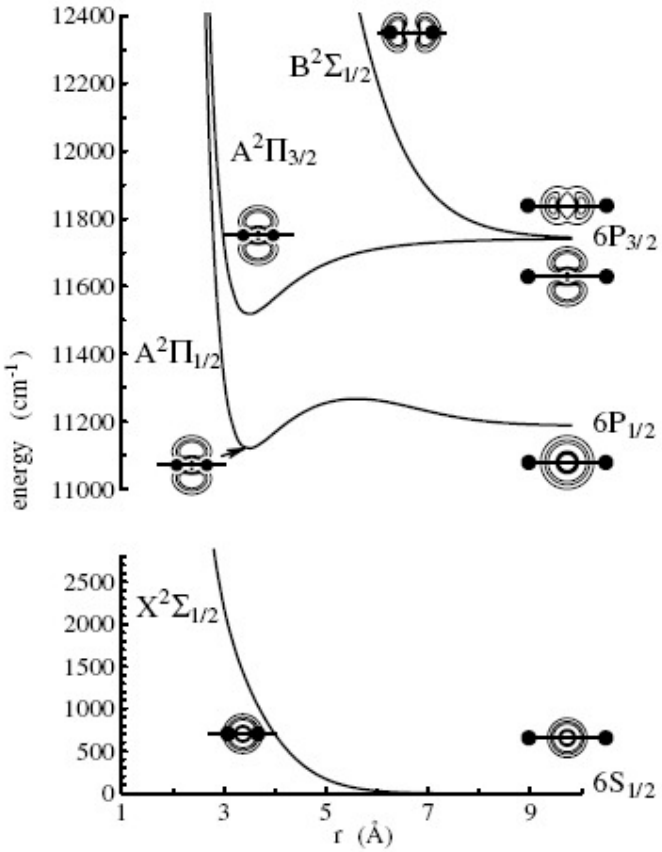

FIG. 2. Adiabatic potentials of the Cs^*He_2 system, including the spin-orbit interaction. The two helium atoms are located at r and $-r$ on the quantization (rotationally symmetry) axis, indicated in the pictographs by a solid line. The shape of the electronic density distribution of the cesium atom changes significantly as helium atoms (filled circles) approach.

The process by which the excited $6P_{3/2}$ state relaxes to the $6P_{1/2}$ state is still an open question. According to the "bubble" model [2,12], a Cs atom in the ground state resides in a spherical cavity (bubble) with a radius of ≈ 7 Å. The excitation of the $6P_{3/2}$ state is followed by a rearrangement of the surrounding helium atoms which are expelled from the volume occupied by cesium valence electron, making the bubble larger and nonspherical. This rearrangement is probably responsible for the fine-structure relaxation in the Cs atom. In contrast to the exciplex formation in a gaseous helium environment [3], the attachment of several helium atoms is not a sequential process. It is likely that the collective motion (oscillation) of atoms in the first solvation shell makes that several atoms can approach the Cs atom simultaneously to form the exciplex.

We calculated the adiabatic potentials and the vibra-tional zero-point energies for all Cs^*He_n systems up to n = 9. The treatment of the molecular vibrations is approximate and will be described in detail elsewhere. Higher vibrational states are not populated at the temperature of the experiments and can he neglected, as well as the contributions from rotations.

As a last step, we have calculated the shape of the emission lines by using the Franck-Condon approximation in a similar way as in [3]. Among all exciplexes considered, the best agreement of the calculated spectra with the experimental ones is provided by those shown in Fig. 1 by solid curves. The shape and width of the line at 10520 cm^{-1} agrees well with the

calculated emission line of Cs($A\Pi_{3/2}$)He_2. However, the pressure shift, i.e., the influence of the surrounding helium matrix was not taken into account. In fact, K. Enomoto et al. [3] measured the emission line of Cs($A\Pi_{3/2}$)He_2 exciplexes in cold helium vapor environment to lie at about 10000 cm^{-1}. We have also observed fluorescence from Cs($A\Pi_{1/2}$)He_2 exciplexes, not discussed here, following $D1$ excitation [13,16]. Such exciplexes were also observed recently on cesium doped He clusters [9].

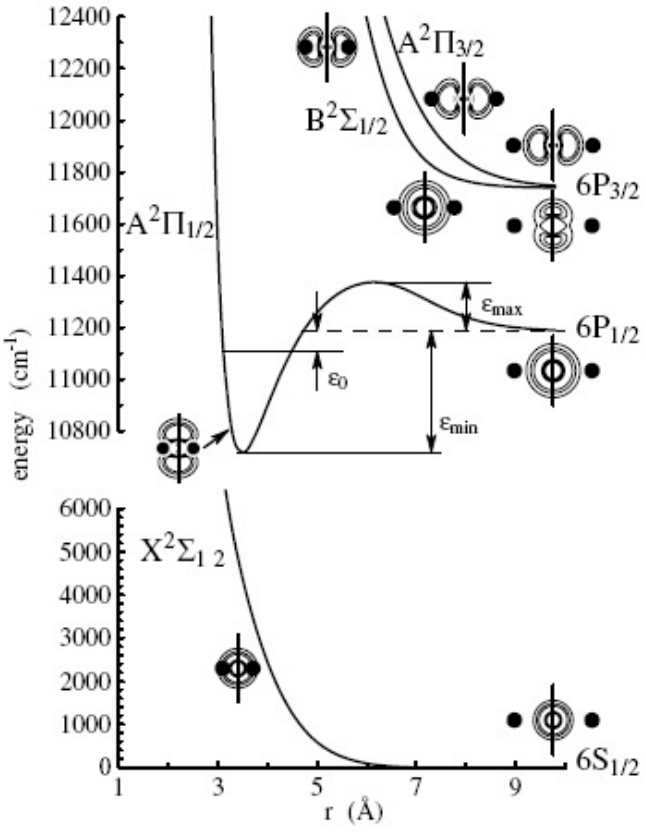

FIG. 3. Adiabatic potentials of the Cs^*He_7 system. The seven helium atoms are located on a ring of radius r concentric with the symmetry axis. Only the $A^2\Pi_{1/2}$ potential has a binding attractive well.

It is clear that the strongest measured peak at 7130 cm^{-1} (Fig. 1) originates from a Cs($A\Pi_{1/2}$)$He_{n>2}$ exciplex, in which the helium atoms form a ring in the nodal plane of the Cs atom. The overall good agreement between calculated and measured lineshapes indicates that it originates from the decay of an exciplex with a specific number n of bound helium atoms and that it is not a superposition of lines from exciplexes with different values of n. Such superpositions were observed in the case of Rb*He_n exciplexes in cold ^{4}He vapor [4]. However, as the ring-shaped exciplexes contain a larger number of helium atoms any imprecision of the initial pair potentials will be amplified. As a consequence the line positions of the higher order Cs*He_n systems cannot he predicted with sufficient accuracy to allow an unambiguous assignment of the observed line. It is very likely that, as in the case of Cs($A\Pi_{3/2}$)He_2 this line experiences a blueshift with helium pressure. Therefore our calculations suggest, as a hest guess, that the observed peak at 7130 cm^{-1} originates from decaying Cs(Cs($A\Pi_{1/2}$)He_7 and not from Cs($A\Pi_{1/2}$)He_6 which is redshifted.

Further evidence for n = 7 comes from the zero-point energies for Cs($A\Pi_{1/2}$)He_n exciplexes ε_0 represented in Fig. 4 by filled circles. Also shown are the depths of the potential minima ε_{min} (open circles) and the heights of the potential barriers ε_{max} (open squares). As is illustrated in Fig. 3, all energies are given with respect to the dissociation limit, i.e., the electronic energy of the $6P_{1/2}$, state. The configuration with n = 8 has the deepest attractive potential, while its zero-point energy due to the stronger localization of helium atoms exceeds the dissociation energy, which makes that complex unstable. There are three possible stable exciplexes Cs($A\Pi_{1/2}$)$He_{5,6,7}$ with a zero-point energy well below the dissociation limit. The bound state with n = 7 has the lowest zero-point energy and therefore should have the largest population.

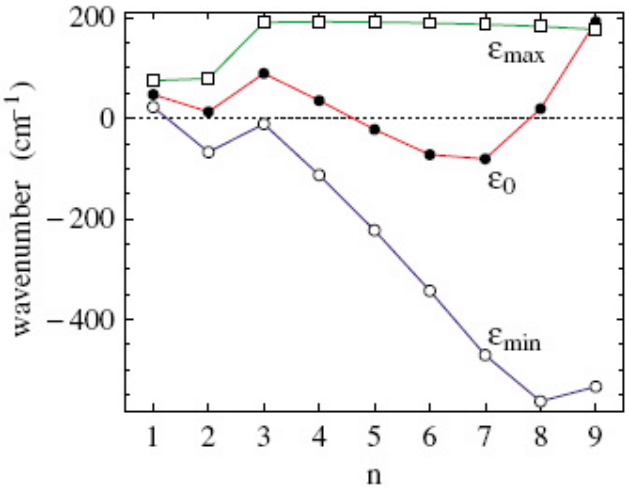

FIG. 4 (color online). Energy dependencies of the $Cs(A\Pi_{1/2})He_n$ exciplexes as a function of the number n of helium atoms. Shown are the minimal energies ϵ_{min} (open circles) of the potential wells, the barrier heights ϵ_{max} (open squares) and the total zero-point energies ϵ_0 (filled circles). All energies are given with respect to the dissociation limit, i.e., the electronic energy of the $6P_{1/2}$ state (see Fig. 3). The temperature of the helium matrix corresponds to $kT = 1.0\ cm^{-1}$.

In summary, we have performed a study of laser induced fluorescence of cesium atoms trapped in the hcp phase of a helium crystal. We have reported the observation of new spectral features, which are broader and more intense than the pure atomic lines. We believe that those lines are formed by the emission from two types of specific Cs^*He_n exciplex structures, viz., an apple-shaped complex with two helium atoms bound to the Cs atom and a dumbbell-shaped complex, in which a ring of helium atoms is bound to the nodal plane of the Cs wave function. These assignments are supported by model calculations, which allow us to obtain the corresponding emission spectra and to analyze the stability of exciplexes. In the case of the ring structure the calculations suggest n = 7 as the most likely number of bound helium atoms.

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*Electronic address: peter.moroshkin@unifr.ch
†Electronic address: www.unifr.ch/physics/frap/

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